DETERMINATION OF THE BIOSOLAR QUALITY BY ANALYSIS CONCENTRATION OF TRACE ELEMENTS USING INDUCTIVELY COUPLED PLASMA OPTICAL EMISSION SPECTROMETRY (ICP OES)

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ABSTRACT

Research on biodiesel quality through the analysis of trace elements concentrations using *Inductively Coupled Plasma Optical Emission Spectrometry* (ICP OES) resulting from commercial biodiesel and of various formulations of blending between biodiesel from palm oil with diesel oil has been done. The study begins with the manufacture of biodiesel through a process of esterification and transesterification reaction with methanol, biodiesel quality analysis, and manufacturing of biodiesel at various blending namely B5, B10, B15, B20, and B25. Trace elements analysis was performed using *Inductively Coupled Plasma Optical Emission Spectrometry* (ICP OES). The research found concentration of trace elements in commercial biodiesel A and commercial biodiesel B dominated by K of 10.68 mg/L and 9,424 mg/L, followed by Mg, Na, Ca, and Fe. Most trace elements in biodiesel B5 is K amounted to 5.846 mg/L, followed by Na, Mg, Ca, and U. Trace elements are most in biodiesel B10 K of 7.113 mg/L, followed by U, Na, Mg, Fe and Ca. Most trace elements in biodiesel B15 is Na amounted to 35.89 mg/L, followed by Fe and Mg. Most trace elements in biodiesel B20 is K amounted to 7.154 mg/L, followed by Na, Ca, Mg, and Fe. Most trace elements in biodiesel B25 is K amounted to 6.154 mg/L, followed by Na, Ca, Mg, and Fe.

Keywords: Biodiesel, ICP OES (*Inductively Coupled Plasma Optical Emission Spectrometry),* trace elements.

1. INTRODUCTION

A reduction in fuel subsidies oil (BBM) by the governments to suppress the national budget deficit and adjust the fuel price with international market prices, directly result in the price of fuel will be more expensive. Fuel made from fossil fuels is classified as a non-renewable (unreneweable). The use of fuel which continuously and tended to increase due to growth in population and industry, while oil reserves who becomes thin and could not be renewed, is highly potential to causethe energy crisis in the future. Therefore, to solve this problem and reduce the dependence on fuel should be a diversified energy by looking for alternative renewable energy (renewable). One of whichis alternative energy derived from plant oils/herbs.

Biodiesel is an alternative fuel for motor vehicles that fuel cell by diesel oil. Biodiesel can be produced from palm oil, soybean and jatropha. Given the oil palm is a plant commonly grown and enough potential to be developed in Indonesia, so that with the increase in oil demand in the transportation sector resulted diesel alternative fuel mixing biodiesel and diesel oil in Indonesia can be pursued [4]. Since 2006, Pertamina has been selling biodiesel with a mixture of 95% diesel and 5% biodiesel [13]. A mixture of biodiesel palm and diesel oil has been commercialized by Pertamina called biodiesel.

The process of making biodiesel is conventionally in general using a vegetable oil transesterification process with short-chain alcohols, using homogeneous catalysts of acid or base, for example H_2SO_4, NaOH, and KOH. Contaminants biodiesel as an element of Na, K, Ca and Mg may affect the performance of the motor and cause corrosion of some components of the motor. These elements led to the formation of deposits and may increase side reactions that contribute to the decomposition of biodiesel. Other elements, such as elements of Ca, Mg and P, which are present in the raw materials used for the production of biodiesel. Other elements can be important due to various factors, such as sulfur can cause acid rain, which was added as an antifoaming silicon in products derived from petroleum can cause decreased motor performance, corrosion, and increases particulate emissions. Determination of inorganic constituents are also important because high concentrations can cause environmental problems and damage to the machine[8] [9] [11].

Determination of trace elements K and Na is very important because some of the biodiesel production process using KOH or NaOH as the catalyst [1]. In addition, the presence of some metals such as Al, Cr, Cu, Fe, Pb, Zn and V in the fuel is not desirable because the metal liberation into the atmosphere on combustion of fuel. Thus, the analysis elements of vegetable oils and biodiesel required to monitor the quality of the fuel [5].

Inductively Coupled Plasma Spectrometry (ICP) is a method based on ion excited and emits light. The intensity of light emitted at specific wavelengths and have the characteristics of certain measurable elements related to the concentration of each element of the sample. Inductive couple plasma (ICP) induction is obtained from alternating current at radio frequency through the coil. Useful for detecting metal content in samples from the environment [14].

2. METHODOLOGY

2.1 Synthesis of Biodiesel from Palm Oil

Crude palm oil in prepared 100 mL. Next, 1.5 mL H_2SO_4 solution was dissolved in 25 mL of methanol until homogeneous (solution 1). Then palm oil and 1 mixed solution gradually at a temperature of 70 ºC for 30 minutes. The mixture was added to funnel to the process of separation between biodiesel and glycerol. In the funnel formed two separate phases, namely biodiesel and triglycerides were dilapisan above as well as methanol and glycerol are dilapisan below. The bottom layer was removed and the top layer was continued for leaching. Washing is done by using warm water. Continue the process of transesterification by reacting back 25 mL of methanol with 1.5 g NaOH at a temperature of 60 °C for 1 hour. After the esterification reaction, do the washing process II, which aims to throw the soap formed, impurities and residual methanol resolve the reaction. Then followed the second separation process was carried out at a temperature of 55 °C, by entering into a funnel where the top layer of the biodiesel and the bottom layer is the remainder of glycerol and methanol. The next stage of purification or drying by heating the biodiesel up to a temperature of 130 °C for 10 minutes.

2.2 Analysis of Physical and Chemical Properties Biodiesel

Analysis of physical properties of biodiesel that analyzes the density of biodiesel.the procedureswere carried out by themethod ASTM D1475. Analysis of the chemical properties of biodiesel arecontent of Free Fatty Acid (% FFA), saponification value and iodine value. Procedures of Free Fatty Acid (% FFA) were based on the AOCS method Ca 5a-40, saponification value was based on AOCS method Cd 3-25, and iodine value was based on Wijsmethod.

2.3 Mixing Biodiesel with diesel (Blending)

Doing variations of blending formulations are B5, B10, B15, B20, and B25. By mixing biodiesel: diesel in various concentrations (5%, 10%, 15%, 20% and 25%) with a pipette biodiesel successive 5 mL, 10 mL, 15 mL, 20 mL, and 25 mL then included into a volumetric flask 100 mL with diesel samples.

2.4 Analysis for Trace Elements on Biodiesel

Determination of Trace Elements was carried out using a Inductively Coupled Plasma Optical Emission Spectrometry (ICP OES). With a sample of biodiesel pipette of 10 mL and inserted into the tube, added with 0.5 mL of HNO_3. The tube is heated above the bath at a temperature of 105 ºC. The samples were cooled and then pipette 10 mL, put in a 25 mL flask and add distilled water up to the mark. The same procedure is performed to sample palm oil, diesel, biodiesel, and biodiesel. Furthermore, the content of all samples analyzed for trace (Trace Elements) by means of Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES).

3. RESULT AND DISCUSSION

3.1 Synthesis of Biodiesel from Palm Oil

Synthesis of biodiesel from palm oil was carried out by esterification, where free fatty acid in palm oil will react with methanol. It is accelerated by the addition of concentrated sulfuric acid catalyst. The result of this esterification produces a turbid mixture. Once the first phase is completed, the synthesis proceed to the second stage which is the transesterification reaction. In this stage, using methanol with the addition of the catalyst NaOH (9% heavy oil).Transesterification reaction time of around 60 minutes with a heating temperature of 60 ºC. Then the reaction product is left for 1 day to form two layers. The bottom layer of yellowish brown which is a layer of glycerol, while the top layer of yellow turbid which is a layer of biodiesel. Having obtained the two layers, the upper and lower layers are separated. The top layer is washed with distilled water to remove impurities and glycerol may be shipped at the time of separation. Furthermore, biodiesel is eliminated residual unreacted methanol by heating in an oven at a temperature of 60 ºC. Subsequently obtained pure biodiesel.

3.2 Analysis of Physical and Chemical Properties Biodiesel

Results of analysis of the density of biodiesel obtained at 0,8654 g/cm^3. Standard density 40 ºC values specified in ASTM D6751 is 0,82 to 0,90 g/cm^3. The results obtained by saponification of biodiesel amounted to 5,2979 mg KOH/g. Saponification biodiesel standards in ASTM D6751 is a maximum of 500 mg KOH/g. Results obtained biodiesel iodine number of 18,9184 g I_2/100g, these results meet the quality standards of ASTM D6751 iodine number that is not more than 115 g I_2/100g.

3.3 Identification of Compounds Biodiesel by Gas Chromatography-Mass Spectroscopy (GC-MS)

The composition of the chemical compounds in biodiesel synthesis result is a 9-octadecanoic methyl ester (methyl ester of oleic) 57.773% and heksadekanoat methyl ester (methyl ester palmitate) 35.579%. Methyl ester obtained in accordance with the content of the fatty acids found in oil-based cooking oil and palm oil are used for biodiesel synthesis, such as oleic acid, palmitic acid, stearic acid and acid arachidat[2], ricinoleic acid derived from palm oil, Ricinoleic esters include esters unique, having the OH group and double chain, has a value lubrisitas the highest among esters.

Table. 1. Compotition Of compound Biodiesel

Peak	Retention Time	% Compound	Compound
1	15,359	0,117	Metil ester dodekanoat
2	17,673	0,832	Metil ester tetradekanoat
3	18,727	0,048	Metil ester pentadekanoat
4	19,504	0,030	Metilheksadekanoat
5	19,549	0,173	Metil ester 9-heksadekanoat
6	19,845	35,579	Metil ester heksadekanoat (metil ester palmitat)
7	20,500	0,033	Metil ester siklopropanoat
8	20,712	0,101	Metil ester heptadekanoat
9	21,548	57,773	Metil ester 9-oktadekanoat(metil ester oleat)

10	21,676	4,299	Metil ester oktadekanoat(metil ester stearat)
11	23,090	0,127	Metil ester risinoleat(metilundekanoat)
12	23,167	0,202	Metil ester 11-eikosanoat
13	23,366	0,416	Metil ester eikosanoat(metilarachidat)
14	24,966	0,076	Metil ester dokosanoat
15	26,213	0,053	Piridin 3-karboxamida
16	26,451	0,089	Metil ester tetrakosanoat

3.4 Analysis for Trace Elements on Biodiesel

Content analysis for trace (Trace Elements) on palm oil, diesel fuel, biodiesel, biodiesel commercially A, biodiesel commercially B, biodiesel B5, B10, B15, B20, and B25 done using ICP-OES for the ability to identify and measure all elements measured by the same in a short time and a high degree of accuracy.

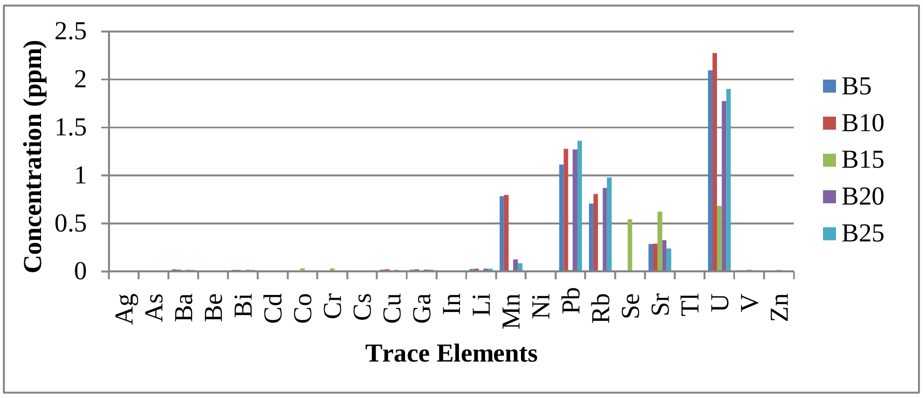

Figure 1. Concentrations of trace elements micro (trace element) (mg / L) in the formulation of blending diesel and biodiesel B5, B10, B15, B20, and B25.

Can be seen in Figure 1, uranium is a trace element that is the highest in the formulation of micro blending diesel and biodiesel B5, B10, B15, B20, and B25 followed by Pb, Rb, and Mn. Uranium derived from diesel oil indicated the existence of which is obtained from petroleum. Solar as a fuel derived from crude oil that is processed in the refineries and separated the results based on their boiling points so as to produce various fuels. Pillay, et al (2012) reported concentrations of uranium in biodiesel 100C and biodiesel 100R around 100 ppm and 70 ppm this is indicated to the differences in the nature of raw materials next of differences in cultivation techniques, soil conditions and plant parts used to make the fuel. The content of Pb, Rb and Mn are also present in the formulation blending diesel and biodiesel B5, B10, B20, and B25.

Abundance of uranium that can be found naturally is uranium-238 (99.275%) and uranium-235 (0.720%) [7]. Uranium was detected probably because the uranium-238 isotope of uranium with the greatest abundance in nature is uranium-238. The existence of uranium in the biodiesel are also reported by Pillay, et al (2012) [11].

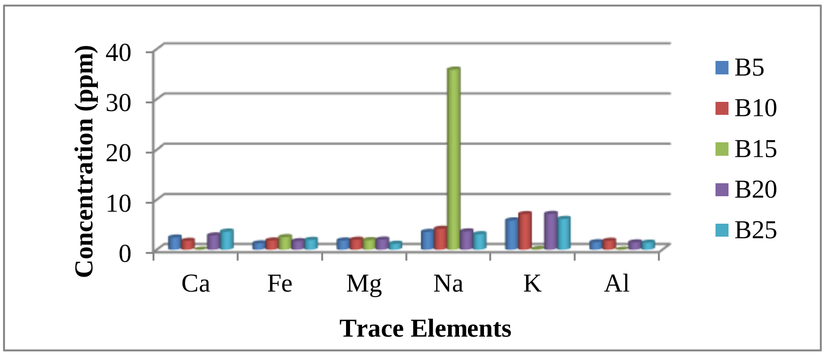

Figure 2. The concentration of trace elements micro (trace element) (mg / L) in the formulation of blending diesel and biodiesel B5, B10, B15, B20, B25

Based on Figure 2, it can be seen that on B15 biodiesel contains elements Na with the highest concentration compared to other biodiesel formulations of this can be caused by biodiesel produced has a high concentration of Na element also in the amount of 34.90 mg / L so that the impact on Na concentration in the formulation blending biodiesel with diesel fuel.

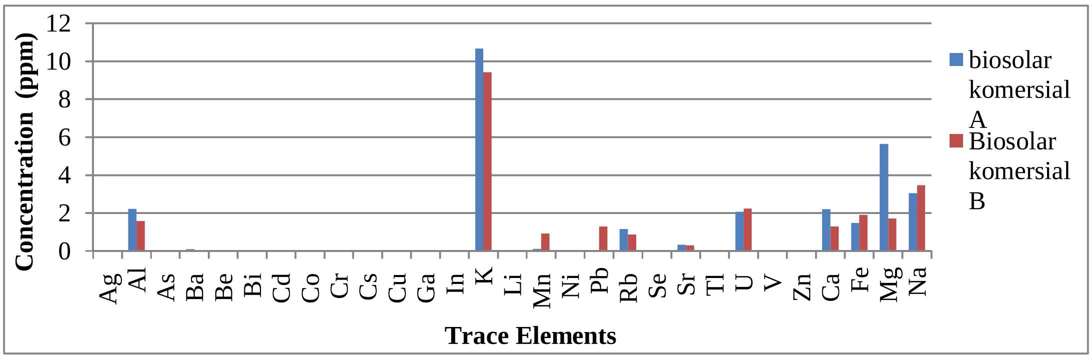

Figure 3. The concentration of trace elements (trace element) (mg/L) in commercial biodiesel A and B commercial biodiesel

Based on Figure 3, it can be seen that the concentration of the element K is the largest element in the commercial biodiesel A and B commercial biodiesel row by 10,68 mg/L and 9,424 mg/L, followed by the elements Mg, Na, Fe, and Ca. Some trace element contained in biodiesel commercially A is Ag amounting to 0,010 mg/L, Al of 2,220 mg/L, As undetectable, Ba amounted to 0,101 mg/L, Be of 0,008 mg/L, Bi amounted to 0,016, K amounted to 10,68 mg/L, U of 2,007 mg/L, Ca of 2,21 mg/L, Fe 1,48 mg/L, Na of 3,034 mg/L as well as commercial biodiesel B is Al of 1,576 mg/L, K of 9,424 mg/L, Mn of 0,928 mg/L, Pb of 1,307 mg/L, U of 2,239 mg/L, Ca amounted to 1,30 mg/L, mg by 1,72 mg/L, Na of 3,472 mg/L. Some trace elements were found in very small quantities. Elements K and Na detected in commercial biodiesel fuel with a high enough concentration. It is indicated for use NaOH or KOH catalyst in the process of making biodiesel mixed with diesel fuel thus affecting the elemental concentrations of K and Na in biodiesel. The high concentrations of K and Na can also be derived from the raw materials for biodiesel are derived from plants [3].

4. CONCLUSION

Based on the research results can be concluded that the potential of palm oil as a raw material for making biodiesel. The quality of biodiesel produced in compliance with the defined quality standards of the American Society for Testing and Materials (ASTM D6751)

The concentration of trace elements (trace elements) in a commercial biodiesel that is in commercial biodiesel A is Al of 2,220 mg/L, K of 10,68 mg/L, Mn of 0,127 mg/L, U of 2,077 mg/L, Ca of 2,21 mg/L, mg of 5,656 mg/L, Na of 3,034 mg/L, and biodiesel commercially B is Al of 1,576 mg/L, K of 9,424 mg/L, Mn of 0,928 mg/L, Pb of 1,307 mg/L, U of 2,239 mg/L, Ca amounted to 1,30 mg/L, mg by 1.72 mg/L, Na of 3,472 mg/L, as well as some other trace elements contained in small amounts. The concentration of trace elements contained in biodiesel commercially most also detected in the formulation of blending biodiesel B5, B10, B15, B20, and B25.

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